FOCUS REVIEW

Generalization of the sacrificial bond principle for gel and elastomer toughening

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Although conventional polymer gels are known as mechanically weak materials, their fracture toughness can be effectively improved by introducing weak and brittle bonds into soft and stretchy polymer networks. This toughening method, denoted as the 'sacrificial bond principle', has been recently proposed by our group. When force is applied to such modified gels with an initial crack, brittle bonds surrounding the crack tip are widely and catastrophically ruptured prior to macroscopic crack propagation. As this extensive brittle bond fracture requires significant energy input, the total energy required for gel fracture is remarkably increased. Since the gel toughness is increased due to sacrificing the introduced brittle bonds, they are termed sacrificial bonds. In this focus review, I describe some extremely tough gels prepared by our group using this principle, e.g., double- or multiple-network gels with high water content featuring covalent sacrificial bonds, self-healing polyampholyte gels containing ionic sacrificial bonds, and PDGI/PAAm gels based on hydrophobic sacrificial bonds exhibiting stress-responsive structural colors.

INTRODUCTION

Polymer gels, or simply gels, are soft and wet materials with large amounts of solvents incorporated in their three-dimensional polymer networks. Owing to this hybrid structure, gels can be microscopically regarded as polymer solutions, while being solids macroscopically. Thus, gels exhibit the properties of both liquids (material permeability, chemical reactivity) and solids (elasticity, self-standing ability). Moreover, the combination of these properties imparts unique additional functionality, e.g., stimuli-responsive volume transition and extremely low surface friction.[1–3] Based on these functions, hydrogels have been extensively utilized as artificial cartilages, drug delivery systems, soft actuators, wound dressings, contact lenses and substrates for tissue engineering.[4–6] These applications require gels to possess sufficient mechanical robustness, e.g., (artificial) knee articular cartilage is continuously exposed to large compression and impact forces for several decades. However, typical gels like jelly or tofu are so brittle that they can easily be fractured by applying a small amount of energy. Therefore, real-life applications require synthetic gels that are soft but mechanically robust, posing a big challenge for material chemists.

The mechanical robustness of materials can be characterized by various parameters, such as tensile or compressive fracture stress, Young's modulus, fracture energy and viscoelastic properties. Among them, fracture energy is an index of toughness and describes resistance against crack propagation, being best suited to describe mechanical robustness, since material failure is a result of crack propagation. Fracture energy (G, J m^{-2}) is defined as the energy required to create a unit area of fracture surface, and the intrinsic fracture energy (G_0) of rubbery materials, including gels, is generally described by the Lake–Thomas theory as

$$G_0 = NU\nu_{area} \qquad (1)$$

where N is the number of chemical bonds in a network strand, U is the dissociation energy of the weakest chemical bond therein (J) and ν_{area} is the area density of elastically effective network strands (m^{-2}).[7,8] Briefly, this theory argues that G_0 of rubbery materials is almost equal to the energy required to fracture network strands across their fracture surface. As gels contain large amounts of solvents, their areal strand density ν_{area} is quite small. Thus, the calculated and measured G_0 values of typical gels are limited to 1–100 J m^{-2}, being much smaller than the values of industrial rubbers, such as carbon black filled rubber (1000–10 000 J m^{-2}).[9] Therefore, wide applications of gels require their additional toughening.

SACRIFICIAL BOND PRINCIPLE

The properties of common hard and tough materials provide a guiding principle for toughening gels. When force is applied to these materials (e.g., metals and plastics) with a notch, an obvious internal structure transition around the crack tip is detected prior to macroscopic crack propagation, exemplified by dislocation of crystals in metals, crazing in polycarbonate and strain-induced crystallization in natural rubbers. For materials exhibiting such structural transitions, G is approximately given by

$$G = hg_{internal} + G_{crack} \qquad (2)$$

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where $g_{internal}$ is the energy required for an internal structural transition of unit volume ($J m^{-3}$), h is the thickness of the zone experiencing this transition (m) and G_{crack} is the fracture energy of the sample after the transition. In this review, the transition zone is denoted as the 'damage zone'. In many cases, $hg_{internal}$ is much larger than G_{crack}, since crack propagation (related to G_{crack}) is a two-dimensional fracture occurring only at the crack tip, whereas the above structural transition is three-dimensional process occurring in the bulk of samples. Thus, the overall fracture energy can be sufficiently increased by structural transitions in the damage zone.[10,11]

Based on the above, our group has proposed applying the sacrificial bond principle to toughen gels and other soft materials,[12] with criteria of designing a tough gel relying on this principle shown in Figure 1a. This model gel features a highly stretchable matrix with a high density of introduced brittle bonds (sacrificial bonds) that should be weaker than the matrix. Figures 1b and c shows possible crack propagation processes in single network and sacrificial bond gels. For a single network gel with a notch, the applied force is concentrated on the network strand nearest to the crack tip, inducing its rupture. After this strand is fractured, the force is transferred to the next strand, and the rupture continues, resulting in global gel fracture. So, just as Lake and Thomas assumed, crack propagation in single network gels mainly results from chain scissions across the fracture interface.[8,13] On the

other hand, sacrificial bond gels are fractured by a different scenario. In this case, brittle sacrificial bonds around a crack are preferentially fractured before the rupture of a stretchable strand at the crack tip. After the wide fracture of these sacrificial bonds, the chain at the crack tip is finally fully stretched and fractured. The wide fracture of sacrificial bonds around the crack tip has a role similar to that of the abovementioned structural transition of tough materials. As described in equation (2), the fracture energy of gels with brittle sacrificial bonds is effectively increased, since additional energy $hg_{internal}$ is required for the formation of a wide damage zone around the crack tip, where the rupture of sacrificial bonds widely occurs.

Theoretically, various kinds of bonds can be sacrificial, e.g., covalent bonds, hydrogen bonds, ionic bonds, and hydrophobic interactions. Our group has synthesized a series of tough hydrogels containing several kinds of sacrificial bonds based on the above principle, with some examples and corresponding toughening mechanisms introduced in this focus review.

DOUBLE-NETWORK GELS

A double-network hydrogel (DN gel) is an original tough gel based on the sacrificial bond principle (Figure 2a).[12,14] Despite a water content of 90 wt%, tough DN gels show high compression fracture stresses of 20 MPa, tensile fracture stresses of 1.5 MPa and fracture energies of 100–4000 $J m^{-2}$, which are comparable to those of some industrial rubbers.[14–16] These gels also successfully resist being hit by a hammer and a golf club, as well as being run over by a large truck (Figure 2b).[17] Tough DN gels comprise two contrasting and well-entangled chemically crosslinked networks; one is very brittle and weak (1st network), while the other is soft and stretchy (2nd network).[18,19] The 1st network is commonly prepared using densely crosslinked strong polyelectrolyte gels, such as poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), with natural polyelectrolytes such as hyaluronic acid and chondroitin sulfate also being suitable.[20,21] Polyelectrolyte gels contain a large amount of counter ions and consequently exhibit significant osmotic pressure, absorbing large amounts of water in aqueous media. This swelling results in diluted and stretched network strands, making the gel weak and brittle. In contrast, the soft and stretchy 2nd network is constructed using sparsely crosslinked neutral gels such as polyacrylamide (PAAm). As neutral gels do not contain counter ions, they do not swell as much in water, consequently preserving their high stretchability. In the case of a tough PAMPS/PAAm DN gel, the 1st brittle PAMPS network exhibits a tensile fracture stress of 0.08 MPa and a tensile fracture strain of 0.36, whereas the 2nd stretchy PAAm network exhibits a fracture stress of 0.16 MPa and a fracture strain of 21.5, being 60 times more stretchable than the 1st network.

If a DN gel containing such contrasting brittle/stretchy DNs is deformed, the internal force first concentrates on the brittle network, inducing its internal fracture prior to global gel fracture. Figure 3a shows systematic uniaxial loading and unloading curves of a DN gel. A significantly large mechanical hysteresis loss was observed during the test, although appearance of the gels was almost unchanged after the test. The observed hysteresis is completely irreversible (even after 2 weeks) and independent of the deformation rate, suggesting that it is caused by the internal rupture of brittle 1st network strands.[22–24] According to calculations based on the above hysteresis loss, 8% of the 1st network strands were ruptured at the breaking point of the stretched DN gel. Furthermore, some tough DN gels exhibit yielding behavior with distinct necking upon uniaxial deformation (Figure 3b).[22,25] Our study implies that the yield point of a DN gel corresponds to the brittle 1st network strands reaching their stretching
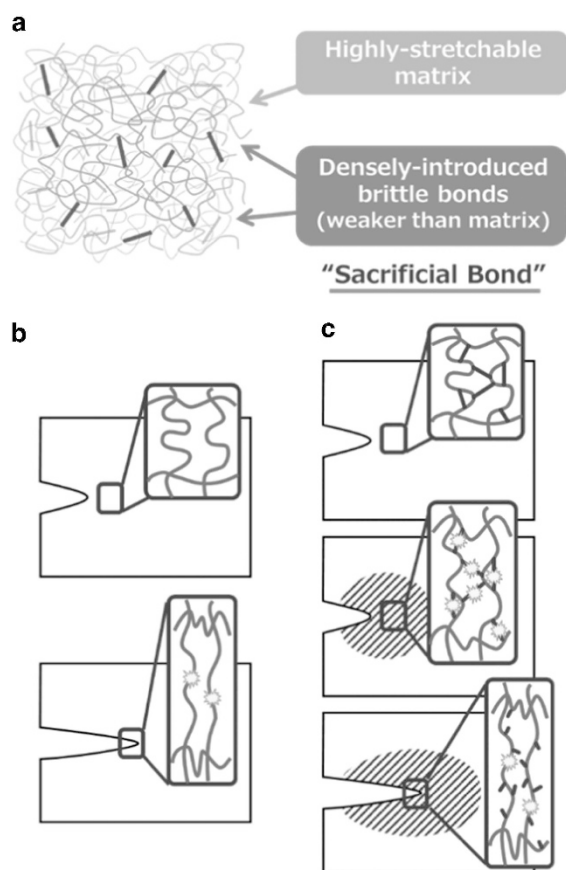

Figure 1 (a) General structure of a tough gel relying the sacrificial bond principle consisting of a highly stretchable matrix with a high density of introduced brittle bonds. (b, c) Possible fracture processes of (b) a single-network gel and (c) a sacrificial bond gel. In the latter case, brittle bonds are widely ruptured prior to macroscopic crack propagation around the crack tip (shadowed zone). A full color version of this figure is available at *Polymer Journal* online.
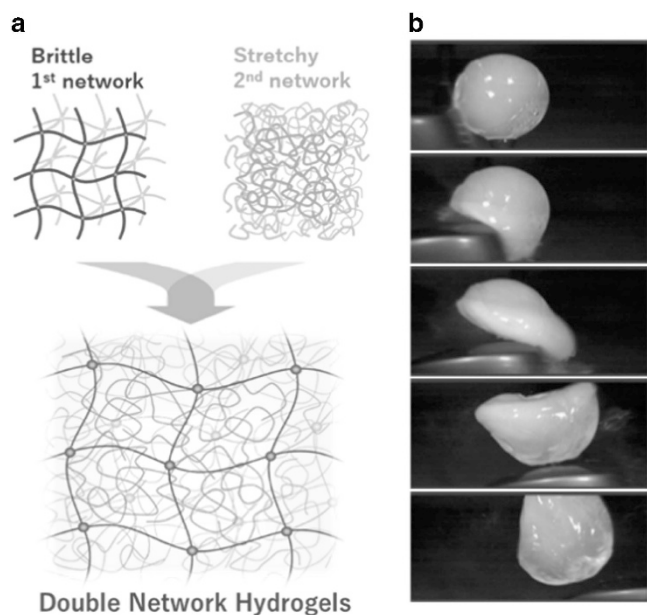
Figure 2 (**a**) An illustration of internal structure of a DN gel consisting of the two contrasting networks and 90 wt% of water. (**b**) A spherical DN gel hit by a golf club. Reproduced from ref. 17 with permission. A movie showing high toughness of DN gels is available at http://altair.sci.hokudai.ac.jp/g2/. A full color version of this figure is available at *Polymer Journal* online.

limit, with the necking process corresponding to catastrophic rupture of the 1st network strands throughout the gel accompanying the extremely large energy dissipation.[26]

The above-mentioned internal fracture of the 1st network implies that the strands embedded in the 2nd stretchy network can act as sacrificial bonds to improve the fracture energy. Based on this idea, Brown[27] and Tanaka[28] independently proposed a DN gel toughening mechanism, as shown in Figure 3c. According to their model, when a DN gel with a notch is stretched, a wide fracture of the 1st brittle network occurs in a damage zone with thickness h around the crack tip prior to macroscopic crack propagation (scission of the 2nd stretchy network). If the energy required to produce a damage zone of unit volume is defined as g_{damage} ($J\,m^{-3}$), the fracture energy (G, $J\,m^{-2}$) of a DN gel can be calculated as

$$G = hg_{damage} + G_{2nd} \qquad (3)$$

where G_{2nd} is the fracture energy of the 2nd network in a DN gel. DN gels exhibit G values of the order of $1000\,J\,m^{-2}$.[16] G_{2nd} has been roughly estimated from the tearing test of the sole PAAm gels as in the order of $10\,J\,m^{-2}$, suggesting that the large fracture energy (high toughness) of DN gels is caused by energy dissipation through internal fracture of the brittle 1st network in the damage zone. The formation of damage zones with thicknesses h of 100–1000 μm was subsequently experimentally confirmed by atomic force microscope measurements and direct microscopic observations (Figures 3d and e), as expected for this model.[29–31] The fracture energy of DN gels is known to be
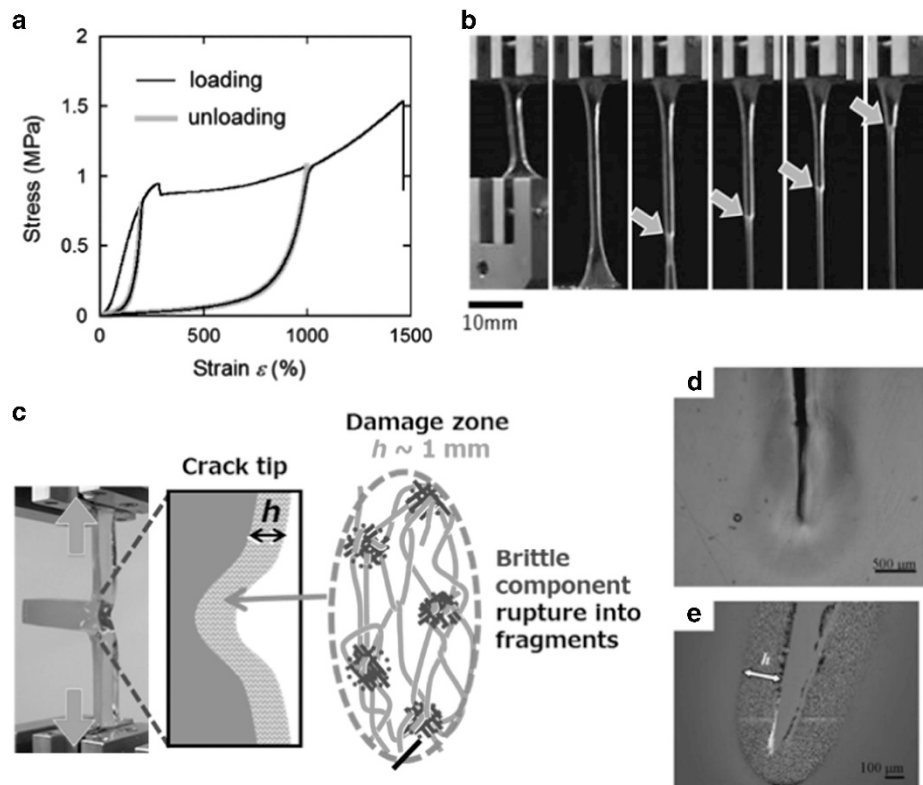

Figure 3 (**a**) Loading and unloading curves of the PAMPS/PAAm DN gel. Large and irreversible mechanical hysteresis is found. Reproduced from ref. 24 with permission from the Royal Society of Chemistry. (**b**) Necking phenomenon of the PAMPS/PAAm DN gel. Reproduced from ref. 25 with permission. (**c**) Possible toughening mechanism of DN gels. Prior to the crack propagation, a wide fracture of the 1st brittle network occurs in a damage zone, which efficiently increases the fracture energy. (**d, e**) The observed damage zone around the crack tip of the DN gel; (**d**) photographic image captured using a conventional optical microscope; (**e**) high-low image captured using a color 3D violet laser scanning microscope. Reproduced from ref. 30 with permission. A full color version of this figure is available at *Polymer Journal* online.
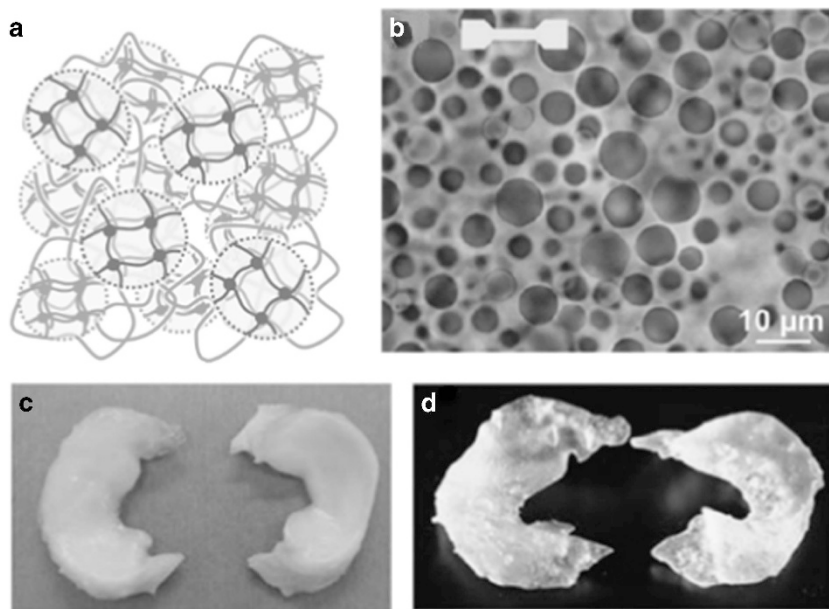
Figure 4 (**a**) Structure illustration of a P-DN gel. (**b**) Microscopic structure of the P-DN gel captured using an optical microscope. Reproduced from ref. 33 with permission. (**c**, **d**) A pair of rabbit meniscus and artificial meniscus made from P-DN gels. Reproduced from ref. 32 with permission from the Royal Society of Chemistry. A full color version of this figure is available at *Polymer Journal* online.
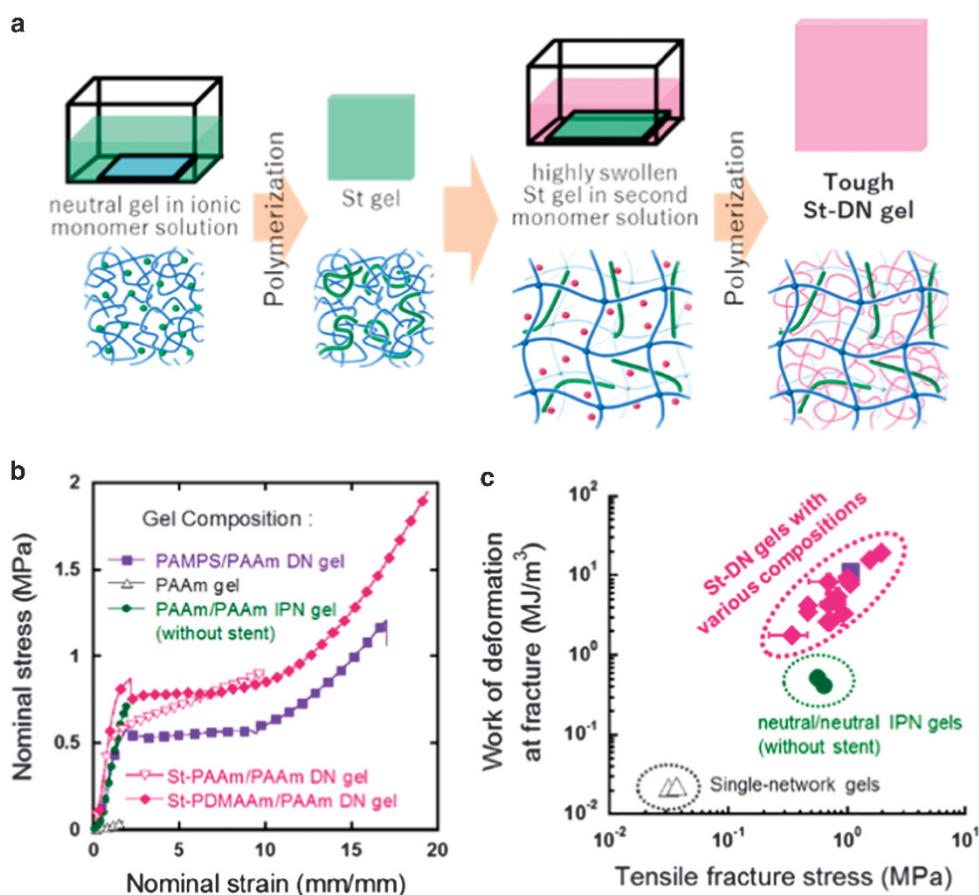

Figure 5 (**a**) Schematic fabrication process of a tough St-DN gels from the neutral 1st network. (**b**) Stress–strain curves of the conventional PAMPS/PAAm DN gel, the PAAm single network gel, the neutral PAAm/PAAm interpenetrating network gel and the St-DN gels. St-DN gels are strong and tough like a conventional DN gel. (**c**) Tensile fracture stress (strength) and work of deformation at fracture (related to toughness) of various gels including St-DN gels from versatile chemical species. Reproduced from ref. 36.
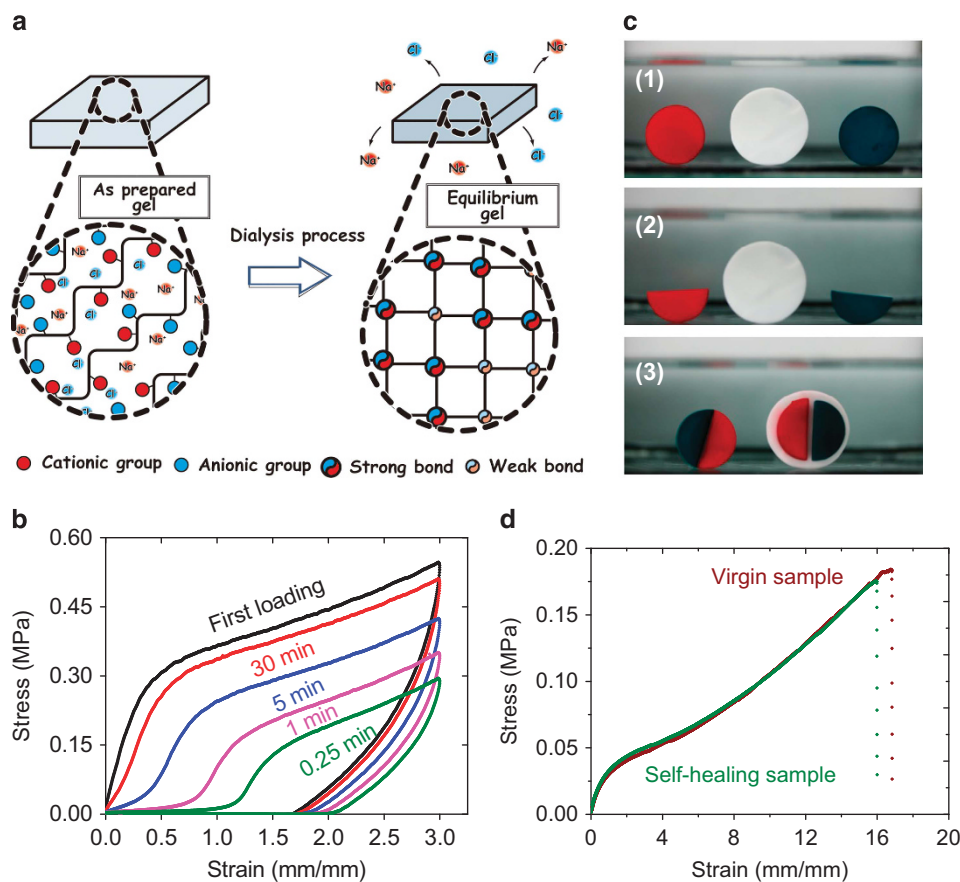
Figure 6 (**a**) Schematic structure of a polyampholyte (PA) hydrogel having strong and weak inter- and intra-molecular ionic bonds. (**b**) Initial and following loading–unloading curves of the PA gel for different waiting times. (**c**) Self-healing of the PA gels between two fresh cut surfaces and adhesion of them. (**d**) Tensile stress–strain curves of a virgin and a self-healed PA gels. Reproduced from ref. 42.

almost proportional to h, confirming the validity of this toughening model.[30]

PARTICLE DN GELS

To obtain tough DN gels containing two independent chemical networks, a two-step gelation process is commonly required.[14] To avoid such complex and long fabrication procedures, we have also investigated particle DN gels that can be synthesized from slurry via single-step gelation (Figure 4a).[32–34] Particle DN gels are also called P-DN or MR gels (microgel-reinforced gels). To prepare a P-DN gel, PAMPS microparticle gels are first prepared by grinding of a bulk PAMPS gel or emulsion polymerization of a precursor solution. Subsequently, the PAMPS gel particles and the 2nd network precursor solution are mixed to prepare a slurry, which is polymerized to form the P-DN gel. Figure 4b shows a microscopic image of a P-DN gel, with its integrated nature preserved by the dispersed 1st network PAMPS particles connected by the stretchy 2nd network. Optimized P-DN gels are sufficiently strong and tough, showing tensile fracture stresses of 2 MPa and fracture energies of 1200 J m^{-2}. Similarly to conventional DN gels, P-DN gels show irreversible mechanical hysteresis upon tensile deformation, suggesting rupture of the 1st brittle network even in the dispersed microparticles. Direct microscopic observation of this fracture process confirmed that the stress is concentrated on brittle particles, effectively inducing the internal fracture of brittle networks.[35] P-DN gels have attracted attention as freely moldable tough gels, since they can be synthesized directly from the slurry. As an example, a P-DN-based artificial articular cartilage of a sheep has been prepared in the shape of its real counterpart (Figures 4c and d).[32]

MOLECULAR STENT METHOD FOR CHEMICAL DIVERSITY OF DN GELS

Practical applications require a technique for preparing tough DN gels from various precursors. However, the 1st network of these gels has been limited to polyelectrolytes due to the following reason. Tough DN gels rely on the synthesis of the weak and brittle 1st network, which is important for inducing internal fracture. As explained above, swelling of polyelectrolyte gels makes them weak and brittle due to the large osmotic pressure induced by counter ions. On the other hand, swollen neutral gels lack counter ions and are typically more robust due to the absence of osmotic pressure and the resulting low swelling degree. Therefore, neutral gels have not been considered as good candidates for the 1st network of tough DN gels.[14] Nevertheless, tough DN gels based on neutral 1st networks have recently been synthesized by introduction of additional components.

Our pioneering investigation of neutral-network-based DN gels led to the discovery of a 'molecular stent method', which is based on the following idea.[36] If a neutral gel can exhibit additional osmotic pressure, its swelling degree should remarkably increase. As a result, such highly swollen neutral gels become weak and brittle and can be used as the 1st network of tough DN gels. In the molecular stent method, linear polyelectrolyte chains or ionic micelles (called
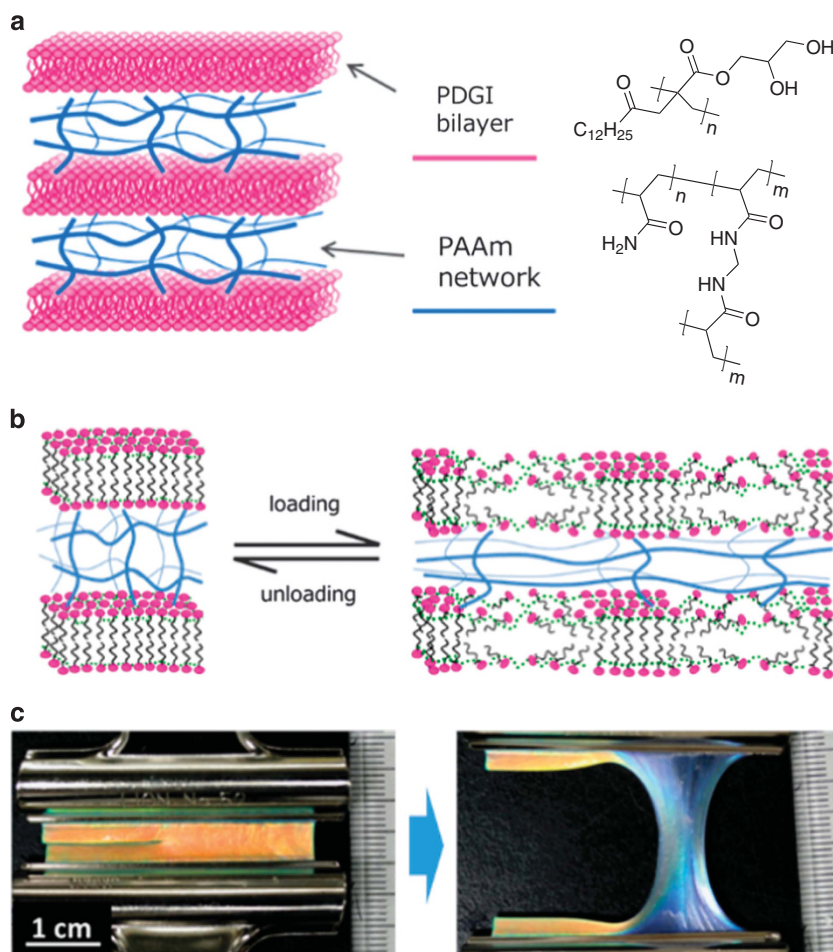
Figure 7 (**a**) Illustration of structure of a PDGI/PAAm hydrogel consisting periodic PDGI laminar bilayers and PAAm gel matrix. (**b**) Possible structure change in a PDGI/PAAm gel upon deformation. Reversible dissociation of PDGI bilayers effectively dissipates large energy. Reproduced from ref. 52 with permission. (**c**) High fatigue resistance and crack blunting of a PDGI/PAAm gel. Reproduced from ref. 55 with permission.

'molecular stents') are introduced into neutral gels. As these trapped ionic components are accompanied by numerous counter ions, the osmotic pressure and swelling degree of the composite neutral gels sufficiently increase. Finally, neutral polymer-based tough DN gels, called St-DN gels, are synthesized by polymerization of the stretchy 2nd network in the swollen neutral network (Figure 5a). When ionic micelles are used as molecular stents, their removal from the produced gel can be achieved by simple diffusion. Figures 5b and c show the results of tensile stress tests and the relationship between tensile fracture stress and work of deformation at the fracture of St-DN gels for various chemical species and other gels, respectively. Single-network gels are weak and not tough, whereas neutral/neutral interpenetrating network gels are strong but still not tough. On the other hand, St-DN gels are both tough and strong regardless of their chemical composition, showing mechanical behavior similar to that of conventional DN gels, i.e., yielding-like behavior and mechanical hysteresis upon tensile deformation.[26,37] This study confirms that weak and brittle networks can also serve as sacrificial bonds in DN gels, expanding their chemical diversity and possible application range. As an example, we prepared bioactive and tough DN gels from neutral polydimethylacrylamide 1st and 2nd networks, utilizing proteoglycan as a molecular stent. As polydimethylacrylamide is a biocompatible polymer, and proteoglycan is a natural polymer, the prepared DN gel should also be biocompatible. Indeed, human umbilical vein endothelial cells grew on the bioactive St-DN gel until reaching confluence, whereas they did not grow well on a conventional PAMPS/PAAm DN gel.[38]

TRIPLE OR MORE NETWORK GELS

The second proposed method for creation of tough DN gels based on neutral 1st networks relies on triple or more networks, with the corresponding gels prepared by gelation of neutral monomers in three or more steps. During the preparation step, the 2nd neutral network is synthesized in the presence of the 1st neutral network. Even though the 2nd network is neutral, the additional component increases internal osmotic pressure, and the swelling degree of the 1st neutral network is sufficiently increased. Thereafter, a 3rd neutral network is synthesized in the presence of the 1st and 2nd networks to obtain triple network (TN) gels. It can be said that the 1st network provides brittle sacrificial bonds, the 2nd network makes the 1st network brittle and the 3rd network acts as a soft and stretchy matrix in the TN gel. The birth of this TN strategy can be traced to a P-DN gel study performed by our group,[33] where P-TN gels were prepared using PAAm neutral microgel particles as the 1st brittle network and bulk PAAm networks as the 2nd and 3rd networks. The obtained fracture energy of this P-TN gel equaled 704 J m^{-2}, being 35 times larger than that of the PAAm single-network gel. Later, Creton and co-workers[39] used this TN strategy for fabricating tough bulk elastomers.
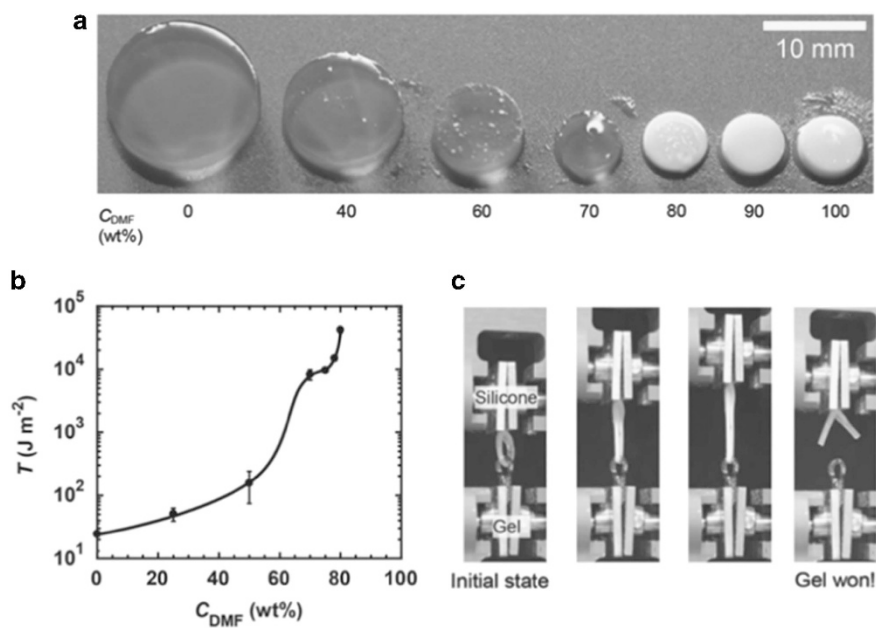
Figure 8 (**a**) Appearance of the *p*-PAAm gels immersed in DMF/water mixture of various DMF concentration C_{DMF}. (**b**) Tearing energy T (J m^{-2}) of the *p*-PAAm gels of various C_{DMF}. The gel with $C_{DMF} = 80$ wt% showed maximum T of 41 600 J m^{-2} while containing 60wt% of solvent. (**c**) A 'Kusa-sumo' match between the *p*-PAAm gel ($C_{DMF} = 80$ wt%) and the silicone rubber thread shows higher strength of the *p*-PAAm gel than the rubber. Reproduced from ref. 56.

Thereafter, Okay and co-workers[40] and Shams ES-haghi and Weiss[41] reported triple and even quadruple-network gels based on neutral polymers. The fracture stress and work of deformation at fracture of these elastomers and gels are sufficiently increased upon incorporation of the 3rd and 4th neutral networks.

TOUGH GELS WITH IONIC SACRIFICIAL BONDS

The toughness of DN or multiple-network gels is due to the irreversible internal fracture of sacrificial bonds. Once mechanical damage accumulates in these gels, it cannot be treated, since covalent bond cleavage is irreversible. To overcome this limitation, the sacrificial bond principle was expanded to systems exhibiting reversible bond formation, e.g., those based on ionic bonds, hydrophobic interactions and hydrogen bonding. Among them, ionic bonds have been most commonly used as reversibly-formed sacrificial bonds. For example, our group prepared a self-healing polyampholyte (PA) gel with high toughness and viscoelasticity by random copolymerization of equal amounts of anionic and cationic monomers with no or little crosslinker.[42] When the as-prepared PA gel (containing ~ 80 wt. % of water) is immersed in pure water, it de-swells due to the formation of inter- or intra-chain ionic bonds, reaching an equilibrium swelling state with a water content of ~ 50 wt.%.[42,43] Optimized PA gels show tensile fracture stresses of 2 MPa and fracture energies of 4000 J m^{-2}. Viscoelastic measurements indicate the existence of two types of multiple ionic bonds inside PA gels: strong bonds with an average activation energy of 308 kJ mol^{-1} and weak bonds with an average activation energy of 71 kJ mol^{-1} (Figure 6a).[42]

PA gels show reversible mechanical hysteresis upon uniaxial deformation. Figure 6b shows the results of cyclic loading–unloading tensile stress tests of a PA gel. Large mechanical hysteresis with some residual strain is observed for the first loading–unloading curve. However, the PA gel completely recovers its original loading curve and length after a 2-h rest. This phenomenon is due to the combination of weak and strong ionic bonds. Weak bonds serve

as reversible sacrificial bonds, breaking during deformation and re-forming at rest, while strong bonds serve as semipermanent crosslinking points, contributing to the elasticity and maintaining the original shape of these gels. When a crack propagates in a PA gel, this reversible energy dissipation can be extensively found around a crack tip, similarly to the internal fracture of DN gels.[42,44] Therefore, PA gels show considerably improved fracture energies compared to conventional gels.

The reversibility of weak bonds adds more unique functions to PA gels, such as self-healing behavior. When two pieces of a PA gel are re-attached, the fracture surface re-joins within a second, and the gel almost completely recovers its original properties after 24-h healing at room temperature (Figures 6c and d). This self-healing behavior is attributed to the fast re-forming of broken brittle bonds.[45] Other features of PA gels attributed to the presence of weak bonds are their high shock absorbability of 95.5%, shape memory and self-adjustable adhesion to charged surfaces, including biological tissues.[42,46]

Such tough gels with hierarchical ionic bonds can be prepared not only by copolymerization of anionic and cationic components but also by combination of polyanions and polycations.[47,48] Tough gels based on ionic sacrificial bonds have also been reported by other groups.[49,50] For example, Suo and co-workers[49] have prepared soft but extremely tough DN hydrogels with an ionically crosslinked 1st network that exhibits partial damage recoverability.

TOUGH GELS BASED ON SOLVOPHOBIC INTERACTIONS

The second example of non-covalent sacrificial bonds is presented by the solvophobic interaction, i.e., an attraction force between solvophobic moieties exposed to solvent. As an example, our group has reported PDGI/PAAm hydrogels based on a mono-domain laminar assembly of poly(dodecyl glyceryl itaconate) (PDGI) embedded into a PAAm gel matrix (Figure 7a).[51,52] The periodic PDGI lamellar bilayers in PDGI/PAAm gels impart bright color that is tunable by various external stimuli, such as stress, pH and temperature.[51–54] The highest

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spatial and time color resolutions of PDGI/PAAm gels equal 0.01 mm and 1 ms, respectively, being comparable to those of typical commercial liquid crystal displays. PDGI/PAAm gels show yielding-like uniaxial deformation behavior with reversible mechanical hysteresis, which is attributed to the rupture of reversible hydrophobic interactions within the PDGI bilayers as weak sacrificial bonds (Figure 7b).[55] PDGI/PAAm gels also show strong fatigue resistance and crack blunting in fracture tests, suggesting the formation of a damage zone around the crack tip, similarly to other tough gels based on the sacrificial bond principle (Figure 7c).

We have also determined that the toughness of common polyacrylamide gels is greatly improved by simple immersion into aqueous solutions of *N,N*-dimethylformamide (DMF).[56] As DMF is a poor solvent for PAAm, PAAm gels shrink and form phase-separated structures in DMF solutions, with the extent of phase separation controlled by the concentration of DMF. In the optimum case, a PAAm gel immersed in 80 wt.% aqueous DMF (*p*-PAAm or phase-separated PAAm gels) showed an extremely high fracture energy of 41 600 J m^{-2} (which, to the best of our knowledge, is the maximum fracture energy among all reported gels without solid fillers), maintaining a solvent content of 60 vol.% (Figure 8a). *p*-PAAm gels immersed in more concentrated DMF solutions were too hard and brittle, whereas those immersed in dilute DMF solutions were stretchy but not as tough. This anomalous toughening of *p*-PAAm gels is triggered by phase separation and not simply by volume shrinkage. Dynamic viscoelastic measurements revealed that the optimized *p*-PAAm gel exhibits a large storage modulus G' and an even larger loss modulus G'', resulting in a high tanδ ($=G''/G'$) value of ~2 at room temperature, although this gel has a percolated chemical PAAm network. This high viscoelasticity is a result of adequate solvophobic interaction between the PAAm chains. During deformation of the optimized *p*-PAAm gel, such moderate interactions are widely destroyed prior to chemical PAAm network fracture, efficiently dissipating energy and significantly improving toughness (Figures 8b and c). The damage accumulated in *p*-PAAm gels can be treated by short thermal annealing or 24-h healing at room temperature. Tough gels based on solvophobic interactions have also been reported by other groups.[57–59]

CONCLUSIONS

The sacrificial bond principle was demonstrated to provide a general method for the synthesis of tough gels. Various types of reversible and irreversible bonds such as covalent bonds, ionic bonds, hydrogen bonds and solvophobic interactions can be used as weak and brittle sacrificial bonds for gel toughening. Difference of such sacrificial bonds gives different mechanical characteristics to the tough gels, i.e., pure elasticity of DN gels from covalent sacrificial bonds and strong viscoelasticity and self-healing property of PA gels from ionic sacrificial bonds. The fracture energies of such tough gels reach 1000–40 000 J m^{-2}, being significantly improved compared with the values of conventional gels (1–100 J m^{-2}) and comparable to those of industrial rubbers. The sacrificial bond principle has also been adopted for toughening of some biological tissues[60,61] and elastomers,[39] enabling diverse applications of gels as load-bearing materials, in particular as artificial articular cartilages strongly bonded to bone, substrates for *in vivo* cartilage regeneration, super-stretchable conductive cables, CO_2 separation membranes and anti-folding coatings protecting against barnacle settlement.[4,62–64]

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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